Articles

Synthesis and Properties of Tetraaza Macrocycles Containing Two 3-Pyridylmethyl, 4-Pyridylmethyl, or Phenylmethyl Pendant Arms and Their Nickel(II) and Copper(II) Complexes: Effects of the Pendant Arms on the Complex Formation Reaction

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Received October 7, 2002

The synthesis and properties of 2,13-bis(3'-pyridylmethyl) (L^3), 2,13-bis(4'-pyridylmethyl) (L^4), and 2,13-bis(phenylmethyl) (L^5) derivatives of 5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$^{1.18}0^{7.12}$]docosane are reported. The 3- or 4-pyridylmethyl groups of $[ML^3](ClO_4)_2$ or $[ML^4](ClO_4)_2$ (M = Ni(II) or Cu(II)) are not involved in coordination, and the coordination geometry (square-planar) and ligand field strength of the complexes are quite similar to those of $[ML^5](ClO_4)_2$, bearing two phenylmethyl pendant arms. However, the complex formation reactions of L^3 and L^4 are strongly influenced by the pyridyl groups, which can interact with a proton or metal ion outside the macrocyclic ring. The macrocycle L^5 exhibits a high copper(II) ion selectivity against nickel(II) ion; the ligand readily reacts with copper(II) ion to form $[CuL^5]^{2+}$ but does not react with hydrated nickel(II) ion in methanol solutions. On the other hand, L^3 and L^4 form their copper(II) and nickel(II) complexes under a similar condition, without showing any considerable metal ion selectivity. The ligands L^3 and L^4 react with copper(II) ion more rapidly than does L^5 at pH 6.4. At pH 5.0, however, the reaction rate of the former macrocycles is slower than that of the latter. The effects of the 3- or 4-pyridylmethyl pendant arms on the complex formation reaction of L^3 and L^4 are discussed.

Key Words : Tetraaza macrocycles, Functionalized macrocycles, Metal complexes, Pyridylmethyl groups, Benzyl groups

Introduction

Polyaza macrocyclic compounds bearing coordinating functional pendant arms have received considerable attention due to their interesting chemical properties and potential applications.[1-19] Recently, some tetraaza macrocyclic ligands bearing N-(2-pyridylmethyl) pendant arm(s) and their transition metal complexes have been prepared and investigated.[8-15] The 2-pyridylmethyl group of such compounds can be coordinated to the central metal ion, and their chemical properties and coordination geometry are influenced by various factors, such as the position and number of the functional groups. Although L^2, L^8, and L^9 bearing two N-(2-pyridylmethyl) groups typically form mononuclear complexes, the fully N-substituted macrocycle L^7 acts as a binucleating ligand.[8,9,12-15] The two pyridyl groups in $[CuL^7]^{2+}$ or $[CuL^8]^{2+}$ are coordinated to the metal ion.[12-14] On the other hand, L^9 forms a five-coordinate complex in which one of the pyridyl groups is not involved in the coordination.[15] It has been also reported that L^2 reacts with Cu^{2+} ion more slowly than does the unsubstituted macrocycle L^1.[12] This observation contradicts those reported for other 14-membered tetraaza macrocycles bearing two or four 2-hydroxyethyl pendant arms.[16,17] Little information, however,
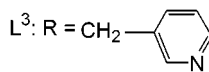
is available on the pyridylmethyl pendant arms role in the kinetic behavior of such macrocycles.[12] We report in the present paper the kinetic behaviors of such macrocyclic
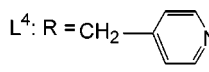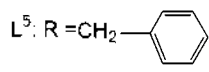

L^1: R =H

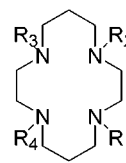L^2: R = CH₂—〔pyridyl〕

L^3: R = CH₂—〔pyridyl〕

L^4: R = CH₂—〔pyridyl〕

L^5: R = CH₂—〔phenyl〕
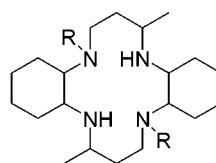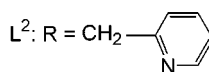
L^6: R = CH₂CH₂CH₃

L^7: R₁ = R₂ = R₃ = R₄ = CH₂—〔pyridyl〕
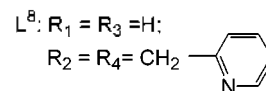
L^8: R₁ = R₃ =H;
R₂ = R₄= CH₂—〔pyridyl〕
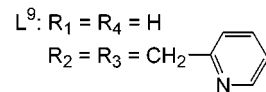
L^9: R₁ = R₄ = H
R₂ = R₃ = CH₂—〔pyridyl〕

compounds bearing 3- or 4-pyridylmethyl groups.

We prepared L^3 and L^4 to investigate the effects of the functional groups upon their complex formation reactions. The macrocycle L^5 containing two phenylmethyl pendant arms was also prepared for comparison. We found that the coordination behaviors and/or the complex formation reactions of L^3 and L^4 are considerably different from those of L^2 or L^5 and are strongly influenced by the nature of the pendant arms. Synthesis and characterization of L^3-L^5 and their nickel(II) and copper(II) complexes are reported, along with the effects of the pendant arms on their chemical properties.

Experimental Section

Measurements. IR spectra were recorded as either Nujol mulls or KBr pellets on a Shimadzu IR-440 spectrophotometer, electronic spectra were recorded with a Shimadzu UV-160 spectrophotometer, and NMR spectra with a Bruker WP 300 FT NMR spectrometer. Conductance measurements were performed with a Metrohm Herisau Conductometer E518. Mass spectra and elemental analyses were performed at the Korea Basic Science Institute, Daegu, Korea. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK-1 magnetic susceptibility balance.

Kinetic measurements for the formation of the copper(II) complexes of the macrocycles were carried out in acetate buffer solutions (pH 5.0-6.4) of methanol-water (1 : 1) mixture at 20 °C. The initial concentrations of the ligands and Cu(NO$_3$)$_2$·3H$_2$O in the reaction mixtures were 1.5×10^{-3} and 3.0×10^{-2} M, respectively. The reaction was monitored using the absorption maxima at 510 (L^1) or 490 nm (L^3-L^5).

Synthesis of the Compounds. L^3: The macrocyclic ligand L^1 was prepared as described previously.[20] A toluene (50 mL) suspension of L^1 (2.0 g, 6.0 mmol), 3-(chloromethyl)-pyridine hydrochloride (3.0 g, 18 mmol), and KOH (4.0 g, 71 mmol) was heated to reflux for more than 30 h and then filtered. The filtrate was evaporated under reduced pressure. The residue was dissolved in minimum volume of chloroform. The solution was filtered and then re-evaporated to dryness. Methanol (20 mL) was added to the resulting residue, and the mixture was allowed to stand several hours. The white precipitate was filtered, washed with methanol, and recrystallized from hot methanol-chloroform (2 : 1). The product was dried in air. Yield: >50%. Mass (*m/e*): 518 (M$^+$). Found: C, 73.75; H, 9.64; N, 15.95. Calc. for C$_{32}$H$_{50}$N$_6$: C, 74.09; H, 9.71; N, 16.20%. IR: 3280 (νN-H), 1600 (νC=N)), and 1580 cm^{-1} (νC=C). ^{13}C-NMR (CDCl$_3$): δ 20.6 (Me), 21.9, 25.5, 25.8, 30.7, 33.2, 49.4, 50.8, 53.8, 55.9, 60.5, 121.9 (Py), 136.5 (Py), 136.8 (Py), 148.6 (Py), and 162.8 (Py) ppm.

L^4: This compound was prepared by a method similar to that for L^3, except that 4-(chloromethyl)pyridine hydrochloride (3.0 g, 18 mmol) was employed instead of 3-(chloromethyl)pyridine hydrochloride. Yield: >50%. Mass (*m/e*): 518 (M$^+$). Found: C, 73.99; H, 9.58; N, 15.98. Calc.

for C$_{32}$H$_{50}$N$_6$: C, 74.09; H, 9.71; N, 16.20%. IR: 3280 (νN-H), 1610 (νC=N), and 1580 cm^{-1} (νC=C). ^{13}C-NMR (CDCl$_3$): δ 20.6 (Me), 22.0, 25.4, 26.3, 30.1, 30.7, 33.2, 50.0, 53.8, 55.0, 60.5, 125.0 (Py), 149.5 (Py), and 151.0 (Py) ppm.

L^5: A chloroform (50 mL) suspension of L^1 (2.0 g, 6.0 mmol), benzyl bromide (1.8 mL, 15 mmol), and KOH (1.0 g, 18 mmol) was heated to reflux for 24 h. The reaction mixture was filtered, and then the filtrate was evaporated to dryness. The residue was re-dissolved in minimum volume of chloroform, and methanol (20 mL) was added to the solution. The mixture was evaporated at room temperature. The white precipitate was filtered, washed with methanol, and recrystallized from hot methanol-chloroform (2 : 1). Yield: >80%. Mass (*m/e*): 517 (M$^+$). Found: C, 79.29; H, 9.94; N, 10.52. Calc. for C$_{34}$H$_{52}$N$_4$: C, 79.02; H, 10.14; N, 10.84%. IR: 3260 (νN-H) and 1605 cm^{-1} (νC=C). ^{13}C-NMR (CDCl$_3$): δ 20.8 (Me), 22.1, 26.5, 26.6, 30.5, 34.2, 46.4, 49.2, 53.6, 60.9, 63.5, 126.0 (Ph), 128.0 (Ph), 128.3 (Ph), and 130.0 (Ph) ppm.

[Ni(H$_2$L^3)](ClO$_4$)$_4$. A methanol suspension (30 cm^3) of Ni(OAc)$_2$·4H$_2$O (2.0 g, 8 mmol) and L^3 (2.0 g, 5 mmol) was heated to reflux for 30 min and then cooled at room temperature. After adding an excess of HClO$_4$, the mixture was stored in a refrigerator until an the orange precipitate formed. The product was filtered and recrystallized from a hot water-acetonitrile (1 : 2) mixture. Yield: ~90%. Found: C, 39.14; H, 5.52; N, 8.57. Calc. for C$_{32}$H$_{52}$N$_6$NiCl$_4$O$_{16}$: C, 39.40; H, 5.32; N, 8.62%. IR: 3190 (νN-H), 1630 (νC=N), and 1580 cm^{-1} (νC=C). ^{13}C-NMR (DMSO-d$_6$): δ 16.6 (Me), 23.9, 25.0, 26.2, 29.2, 29.8, 46.0, 46.3, 49.0, 55.8, 74.3, 125.3 (Py), 130.1 (Py), 142.9 (Py), 147.4 (Py), and 149.3 (Py) ppm. Magnetic moment (μ_{eff}): 0.21 μB.

[Cu(H$_2$L^3)](ClO$_4$)$_4$·2H$_2$O. An orange-red complex was prepared by a method similar to that for the nickel(II) complex [Ni(H$_2$L^3)](ClO$_4$)$_4$, except that Cu(OAc)$_2$·H$_2$O (2.0 g, 8 mmol) was reacted instead of Ni(OAc)$_2$·4H$_2$O. Yield: ~90%. Found: C, 37.76; H, 5.48; N, 8.35. Calc. for C$_{32}$H$_{56}$N$_6$CuCl$_4$O$_{18}$: C, 37.82; H, 5.50; N, 8.27%. IR: 3480 (νO-H, H$_2$O), 3180 (νN-H), 1630 (νC=N), and 1580 cm^{-1} (νC=C).

[Ni(H$_2$L^4)](ClO$_4$)$_4$. An orange complex was prepared by a method similar to that for [Ni(H$_2$L^3)](ClO$_4$)$_4$, except that L^4 was reacted instead of L^3. Yield: ~90%. Found: C, 39.08; H, 5.48; N, 8.70. Calc. for C$_{32}$H$_{52}$N$_6$NiCl$_4$O$_{16}$: C, 39.40; H, 5.32; N, 8.62%. IR: 3180 (νN-H), 1620 (νC=N), and 1580 cm^{-1} (νC=C).

[Cu(H$_2$L^4)](ClO$_4$)$_4$·2H$_2$O. An orange-red complex was prepared by a method similar to that for [Ni(H$_2$L^3)](ClO$_4$)$_4$, except that L^4 and Cu(OAc)$_2$·H$_2$O (2.0 g, 8 mmol) were reacted instead of L^3 and Ni(OAc)$_2$·4H$_2$O, respectively. Yield: ~90%. Found: C, 37.95; H, 5.56; N, 8.24. Calc. for C$_{32}$H$_{56}$N$_6$CuCl$_4$O$_{18}$: C, 37.82; H, 5.50; N, 8.27%. IR: 3490 (νO-H, H$_2$O), 3190 (νN-H), 1620 (νC=N), and 1580 cm^{-1} (νC=C).

[ML](ClO$_4$)$_2$ (M=Ni(II) or Cu(II); L=L^3 or L^4). To a saturated water-acetonitrile (1 : 3) solution of the protonated complex [M(H$_2$L)](ClO$_4$)$_4$ (1.0 g) was added 1.0 M NaOH solution (5.0 mL). After the addition of an excess of

$NaClO_4$, the solution was stored in a refrigerator, forming orange and orange-red solids. The product was filtered, washed with methanol, and dried in air. Yield: >80%. **[NiL³](ClO₄)₂**. (Found: C, 48.89; H, 6.43; N, 10.93%. Calc. for $C_{32}H_{50}N_6NiCl_2O_8$: C, 49.51; H, 6.49; N, 10.82%. IR: 3190 (νN-H), 1610 (νC=N), and 1580 cm^{-1} (νC=C). Magnetic moment (μ_{eff}): 0.21 μB.) **[CuL³](ClO₄)₂**. (Found: C, 48.85; H, 6.40; N, 10.82%. Calc. for $C_{32}H_{50}N_6CuCl_2O_8$: C, 49.20; H, 6.45; N, 10.76%. IR: 3210 (νN-H), 1600 (νC=N), and 1580 cm^{-1} (νC=C).) **[NiL⁴](ClO₄)₂**. (Found: C, 49.25; H, 6.45; N, 10.95%. Calc. for $C_{32}H_{50}N_6NiCl_2O_8$: C, 49.51; H, 6.49; N, 10.82%. IR: 3190 (νN-H), 1600 (νC=N), and 1580 cm^{-1} (νC=C). Magnetic moment (μ_{eff}): 0.17 μB.)

[CuL⁴](ClO₄)₂. (Found: C, 49.05; H, 6.42; N, 10.80%. Calc. for $C_{32}H_{50}N_6CuCl_2O_8$: C, 49.20; H, 6.45; N, 10.76%. IR: 3210 (νN-H), 1600 (νC=N), and 1580 cm^{-1} (νC=C).)

[NiL⁵](ClO₄)₂. An ethanol suspension (30 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (2.0 g) and $CH(OEt)_3$ (6.0 mL) was refluxed for 2 h. After the addition of L⁵ (1.0 g), the mixture was refluxed for 10 h and cooled to room temperature. An excess of $NaClO_4$ or $HClO_4$ dissolved in water (*ca.* 20 mL) was added to the reaction solution. The orange solid, that was precipitated, was filtered, washed with methanol, and recrystallized from hot DMSO-water (2 : 1). Yield: >80%. Found: C, 52.79; H, 6.73; N, 7.37%. Calc. for $C_{34}H_{52}N_4NiCl_2O_8$: C, 52.73; H, 6.77; N, 7.23%. IR: 3190 (νN-H), 1610 (νC=C), and 1590 cm^{-1} (νC=C). ^{13}C-NMR (CD_3NO_2): δ 17.8 (Me), 25.4, 26.0, 26.1, 32.4(*d*), 41.2, 49.0, 51.3, 57.0, 58.6, 131.3 (Ph), 131.5 (Ph), 131.7 (Ph), and 134.4 (Ph) ppm.

[CuL⁵](ClO₄)₂. A red complex was prepared by a method similar to that for the nickel(II) complex [Ni(H₂L³)](ClO₄)₄, except that L⁵ and $Cu(OAc)_2 \cdot H_2O$ (2.0 g, 8 mmol) were reacted instead of L³ and $Ni(OAc)_2 \cdot 4H_2O$, respectively. Yield: >80%. Found: C, 52.32; H, 6.70; N, 7.32%. Calc. for $C_{34}H_{52}N_4CuCl_2O_8$: C, 52.41; H, 6.73; N, 7.19%. IR: 3170 (νN-H), 1610 (νC=C), and 1590 cm^{-1} (νC=C).

Results and Discussion

Synthesis and Characterization. The di-*N*-substituted macrocycles L³-L⁵ were prepared by the direct reaction (*see* Experimental Section) of L¹ with corresponding alkylating agents. The formation of L³-L⁵ is associated with the reported trend that the two sterically less hindered amino groups of L¹ are selectively alkylated.[12,13,19,21,22] The macrocycles L³-L⁵ readily dissolved in chloroform but not in methanol at room temperature. The mass, ^{13}C NMR, and infrared spectra of the compounds are listed in the Experimental Section, along with elemental analyses.

The reaction of L³ or L⁴ with $M(OAc)_2 \cdot nH_2O$ (M=Ni(II) or Cu(II); *n*=1 or 4) in methanol, followed by the addition of $HClO_4$ (pH > 3.0), produces the protonated complexes [M(H₂L³)](ClO₄)₄ or [M(H₂L⁴)](ClO₄)₄ (H₂L=a diprotonated form of L) in which the 3- or 4-pyridylmethyl groups are protonated. The complexes are readily deprotonated to [ML³](ClO₄)₂ or [ML⁴](ClO₄)₂ in basic conditions (pH=10-11). The copper(II) complex [CuL⁵](ClO₄)₂ containing two

N-benzyl pendant arms can also be prepared by the reaction of the macrocycle with $Cu(OAc)_2 \cdot H_2O$ in methanol, as usual. However, somewhat unexpectedly, the nickel(II) complex of L⁵ could not be prepared from the direct reaction (reflux >20 h) of the hydrated salt $Ni(OAc)_2 \cdot 4H_2O$ with the macrocycle in methanol or ethanol; addition of $HClO_4$ or $NaClO_4$ to the reaction solution produced only the white solid [H₂L⁵](ClO₄)₄. This means that L⁵ is highly selective for complex formation with Cu(II) over Ni(II) ion in solutions containing water. The complex [NiL⁵](ClO₄)₂ can be prepared only under dehydrated condition (*see* Experimental Section: $HC(OEt)_3$ reacts with H_2O to yield HCO_2Et and EtOH).[23,24] The high selectivity of L⁵ in the complex formation of copper(II) over nickel(II) ion in solutions containing water may result from the difference in acidity between the two metal ions (Cu(II) > Ni(II)) and/or due to the presence of the bulky hydrophobic benzyl pendant arms, which inhibits the coordination of the hydrated metal ion.[25,26]

The complexes [ML](ClO₄)₂ (M=Ni(II) or Cu(II); L=L³, L⁴, or L⁵) are soluble in nitromethane and acetonitrile but are nearly insoluble in water at room temperature. In acidic solutions, the 3- or 4-pyridylmethyl groups of [ML³](ClO₄)₂ and [ML⁴](ClO₄)₂ are protonated to form [M(H₂L³)](ClO₄)₄ and [M(H₂L⁴)](ClO₄)₄, respectively. This result is quite different from the reported trend that the coordinated 2-pyridylmethyl groups of [ML²](ClO₄)₂ are highly resistant to protonation.[12] The protonated complexes as well as [ML⁵](ClO₄)₂ are quite stable in the solid state and decomposed very slowly even in concentrated acid solutions. Visible spectra of the complexes (1.0 × 10^{-3} M) in 0.3 M $HClO_4$ acetonitrile-water (1 : 1) indicated that only less than 3% of the complexes are decomposed in 20 h at 25 °C. The infrared spectra of the complexes are similar to those of the free ligands, except that $\nu(ClO_4)$ of the counter anions is observed at *ca.* 1100 cm^{-1}. The molar conductance values

Table 1. Electronic Absorption Spectral Data of the Complexes^a

Complex	λ_{max}, nm (ε, M^{-1} cm^{-1})	Λ_M, Ω^{-1} mol^{-1} cm^2	
[NiL¹]$^{2+}$ ^{b}	463(73)	465(66)^c	
[NiL²]$^{2+}$ ^{d}	530(6.0)	527(6.4)^c	
[Ni(H₂L³)](ClO₄)₄	489(110)	488(103)^c	300	535^c
[NiL³](ClO₄)₂	483(98)	484(95)^c	135	245^c
[Ni(H₂L⁴)](ClO₄)₄	488(90)	490(86)^c	285	510^c
[NiL⁴](ClO₄)₂	485(115)	483(110)^c	130	240^c
[NiL⁵](ClO₄)₂	480(108)	482(110)^c	140	73^c
[NiL⁶]$^{2+}$ ^{f}	484(109)	486(103)^c	
[CuL¹]$^{2+}$ ^{b}	487(113)	508(150)^c	
[CuL²]$^{2+}$ ^{d}	554(111)	553(109)^c	
[Cu(H₂L³)](ClO₄)₄	475(290)	530(277)^c	340	565^c
[CuL³](ClO₄)₂	470(285)	490(270)^c	130	255^c
[Cu(H₂L⁴)](ClO₄)₄	478(275)	534(265)^c	268	540^c
[CuL⁴](ClO₄)₂	470(295)	490(270)^c	300	535^c
[CuL⁵](ClO₄)₂	470(270)	505(240)^c	155	70^c
[CuL⁶]$^{2+}$ ^{g}	486(234)^c		

^{a}In nitromethane at 20 °C unless otherwise specified. ^{b}Ref. 20. ^{c}In acetonitrile. ^{d}Ref. 12. ^{e}In DMSO. ^{f}Ref. 21. ^{g}Ref. 23.

(Table 1) of $[ML](ClO_4)_2$ measured in nitromethane (130-160 $\Omega^{-1}mol^{-1}cm^2$), acetonitrile (240-260 $\Omega^{-1}mol^{-1}cm^2$), and/or DMSO (*ca.* 70 $\Omega^{-1}mol^{-1}cm^2$) indicate that the complexes are 1 : 2 electrolytes. The values of $[M(H_2L^3)](ClO_4)_4$ and $[M(H_2L^4)](ClO_4)_4$ measured in nitromethane (265-340 $\Omega^{-1}mol^{-1}cm^2$) and acetonitrile (510-540 $\Omega^{-1}mol^{-1}cm^2$) correspond to 1 : 4 electrolytes. Visible absorption spectra (Table 1) of the nickel(II) and copper(II) complexes of L^3 and L^4 measured in nitromethane are quite similar to those of L^5, H_2L^3, and H_2L^4. The wavelengths (*ca.* 485 and 475 nm for the nickel(II) and copper(II) complexes, respectively) and molar absorption coefficients of the bands are also comparable with those reported for other square-planar complexes, such as $[ML^6]^{2+}$ bearing two *N*-propyl groups, but are quite different from those of the octahedral complexes $[ML^2]^{2+}$, in which two 2-pyridylmethyl groups are coordinated to the metal ion.[12,21,23] This leads to the conclusion that the nickel(II) and copper(II) complexes of L^3-L^5 have a square-planar coordination geometry. In the case of the copper(II) complexes, the wavelengths of the *d-d* bands measured in coordinating solvents, such as acetonitrile, are somewhat longer than those in nitromethane, a non-coordinating solvent. This can be attributed to the solvent coordination to the metal ion. It is clear that the nitrogen atoms of the 3- or 4-pyridylmethyl groups in $[ML^3](ClO_4)_2$ and $[ML^4](ClO_4)_2$ are not involved in intra-molecular coordination, and the coordination geometry and ligand field strength of the complexes are quite similar to those of $[ML^5](ClO_4)_2$.

Effects of the Pyridylmethyl Groups on the Complex Formation Reactions. As described above, the nickel(II) complex of L^5 containing two *N*-phenylmethyl pendant arms could not be prepared by the direct reaction of the hydrated metal ion with the macrocycle. The electronic absorption spectra of the reaction mixture also showed no apparent spectral change during several days. Such behavior of L^5 is quite different from that of the di-*N*-propylated macrocycle L^6, which easily reacts with hydrated nickel(II) ion to form the square-planar complex $[NiL^6]^{2+}$,[21,23] and can be explained in correlation with the severe steric hindrance caused by the bulky benzyl groups. In the cases of L^3 and L^4, however, their square-planar nickel(II) complexes could be prepared readily by the direct reaction of the macrocycles with the hydrated metal ion (*see* Experimental Section), in spite of the fact that the steric effect of the pyridylmethyl groups are not quite different from that of the phenylmethyl groups in L^5. It can be suggested that the complex formation of L^3 or L^4 is assisted by the pre-coordination of the pyridyl groups to the hydrated metal ion outside the macrocyclic ring,[16,17] even though the pendant arms are not involved in coordination in the resulting complex.

Pseudo first-order rate constants (*k*) for the reaction of Cu^{2+} with L^3-L^5 were determined under the condition of sodium acetate buffer solutions (pH 5.0-6.4) at 25 °C. (It is likely that the predominant forms of L^1-L^5 involved in the reactions at pH 6.4-5.0 are diprotonated species, in which two amino groups on the macrocyclic rings are protonated.)[16,23] Table 2 shows that the introduction of the pyridylmethyl or

Table 2. Pseudo-First Order Rate Constants (*k*) for the Reaction of Cu^{2+} Ion with the Macrocyclic Ligands in Acetate Buffer Solutions[a]

Ligands	k, sec^{-1} ($t_{1/2}$, sec)		
	pH 6.4	pH 5.9	pH 5.0
L^1	-0.1	7.6×10^{-2} (9)	1.2×10^{-2} (58)
L^2		1.6×10^{-3} [b]	
L^3	*ca.* 0.1 (7)	3.0×10^{-2} (23)	3.2×10^{-3} (217)
L^4	-0.1	4.6×10^{-2} (15)	4.7×10^{-3} (147)
L^5	4.1×10^{-2} (16)	3.2×10^{-2} (22)	9.6×10^{-3} (72)

[a]Measured in methanol-water (1 : 1) mixture at 25 °C. $|Cu^{2+}| = 3.0 \times 10^{-2}$ *M*. [Ligand] = 1.5×10^{-3} *M*. [b]Measured at pH 5.7; ref. 12.

phenylmethyl groups into L^1 to give L^3-L^5 reduces the reaction rate. This result can be attributed to the steric hindrance of the *N*-substituents.[12] In all cases, the reaction rate becomes slower with decreasing pH, as usual. Interestingly, the effect of pH on the rate of L^3 and L^4 is much stronger than that of L^5, and the *k* values decrease in the orders of $L^4 > L^3 > L^5$ at pH 6.4, $L^4 > L^3 \sim L^5$ at pH 5.9, and $L^5 > L^4 > L^3$ at pH 5.0. The faster reaction rate of L^3 or L^4 at pH 6.4, compared with that of L^5, may be a consequence of the fact that the 3- or 4-pyridylmethyl groups promote the reaction by providing the points of the attachment outside the macrocyclic ring for the metal ion. The pyridyl groups of L^3 and L^4 are protonated in acid solutions, and the resulting pyridinium groups cannot bind to the metal ion. One of the reasons for the relatively slow reaction rate of L^3 and L^4 at lower pH (5.0) may be the higher proportion of the protonated species. The smaller *k* values of L^3 and L^4 at pH 5.0, compared with that of L^5, also supports the suggestion that the pyridinium groups exhibit severer steric hindrance than do the phenylmethyl groups. The *k* values (3.2×10^{-3}-4.6×10^{-2} sec^{-1}) for L^3 and L^4 measured at pH 5.0-5.9 are larger than that reported for L^2 (1.6×10^{-3} sec^{-1} at pH 5.7).[12] This strongly indicates that the reaction rate is also affected by the isomeric structure of the pyridylmethyl groups. Unfortunately, we could not obtain the kinetic data at pH > 6.4 because the reaction rate was too fast to measure by the ordinary methods. Therefore, the effects of the pyridylmethyl groups on the complex formation of L^2-L^4 are not thoroughly understood at this time. However, the order of the reaction rate ($L^2 < L^3 < L^4$) in the acidic conditions corresponds to the expectation that the steric hindrance caused by the protonated pyridylmethyl groups decreases in the order of $L^2 > L^3 > L^4$.

The above results show that the introduction of either the pyridylmethyl or the phenylmethyl pendant arms into L^1 to give L^3-L^5 increases the steric congestion around the macrocyclic ring and retards the complex formation reaction. Although the 3- or 4-pyridylmethyl groups of $[ML^3]^{2+}$ and $[ML^4]^{2+}$ are not involved in coordination, the complex formation reaction is significantly influenced by the pre-coordination and/or protonation of the pendant arms.

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